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Description

This invention relates to multilayer polypropylene films.

5 Biaxially-stretched films of crystalline polypropylene are widely used for packaging, making the best use of the transparency and rigidity thereof. Though such films themselves have heat sealing properties, they are not generally as they are since a very high temperature is required for heat sealing and shrinkages or wrinkles may be formed. For preference, there are used multi-layer films formed by coating on or laminating to one or both sides of the crystalline film a resin capable of being heat sealed at lower temperatures or by coextruding the film and the resin. An important characteristic required of this heat
10 sealing resin is that its heat sealing temperature be sufficiently low, because the lower the heat sealing temperature, the higher the possible speed of packaging becomes.

However, mere lowering of the heat sealing temperature is not sufficient, and such properties as transparency, scratch resistance and hot tack are, of course, also important. When it is intended to use the film for packaging, the amount of solvent-extractibles must be small. Furthermore, it is desired that
15 properties such as slip, blocking resistance and the like be good.

Although various heat sealing resins have been proposed, no heat sealing resin has been obtained which meets all the requirements mentioned above. For example, a polypropylene film having laminated thereto polyethylene or an ethylene-vinyl acetate copolymer has relatively good low-temperature heat sealing properties, but these properties do not reach a satisfactory level, and moreover, the laminated film
20 is inferior in transparency and scratch resistance. The polypropylene resin includes a propylene/ethylene random copolymer in which the bound ethylene content is about 5% by weight; however, this copolymer is greatly inferior in low-temperature heat sealing properties and also inferior in hot tack, though it has good transparency, scratch resistance and blocking resistance properties.

When the bound ethylene content of the propylene/ethylene random copolymer is increased to improve
25 its low-temperature heat sealing property, this property is somewhat improved but the transparency and blocking resistance are reduced.

Among the polypropylene resins, propylene/butene-1 copolymers have long been known as heat sealing resins (see GB-A-1,018,341. Japanese Laid-Open Patent Applications Nos. 128,781/75, 17,542/80, 66,990/79, 114,887/78, 22,307/81 and 166,455/85). However, most of these copolymers are tacky, inferior in
30 blocking resistance, scratch resistance and slip, and the amount of solvent-extractibles is large. Even those which have relatively good transparency, scratch resistance and blocking resistance are still not adequately satisfactory in low-temperature heat sealing property.

To overcome these defects, the blending of isotactic polypropylene in a small or large amount with the propylene/butene-1 copolymers is disclosed in Japanese Laid-Open Patent Applications Nos. 58,861/81, 48,846/79. If too little isotactic polypropylene is blended, the improvement in blocking resistance and
35 scratch resistance is insufficient, the film obtained is inferior in slip and the amount of the solvent-extractibles is large. On the other hand, if there is too much isotactic polypropylene, the advantage of low-temperature heat sealing property is reduced, and the film obtained still has the problem that it is inferior in block resistance, slip and hot tack and contains a large amount of solvent-extractibles.

40 It is an object of the invention to provide a multi-layer polypropylene film having good low-temperature heat sealing properties, transparency, scratch resistance and hot tack and having a small amount of solvent-extractibles, and, preferably, also having good slip and blocking resistance.

It has now been found, in accordance with the present invention that the above objectives may be achieved with a multi-layer polypropylene film comprising a substrate layer formed of crystalline propylene
45 random copolymer, (B) a copolymer of polypropylene having laminated thereto a binary or a ternary blend consisting essentially of specific proportions of (A) a specific propylene and an α -olefin having four or more carbon atoms or a specific copolymer of propylene, an α -olefin having four or more carbon atoms and ethylene; and, optionally (C) a highly crystalline polypropylene.

According to the invention, therefore, there is provided a multi-layer polypropylene film which com-
50 prises a crystalline polypropylene substrate layer having laminated to at least one side thereof a film of a resin composition comprising:

(A) 10-90% by weight of a propylene random copolymer which:

- (i) has comonomer content of 4-15% by weight,
- (ii) has a Vicat softening point of 122°C or less, and

55 (iii) has a cold xylene-soluble portion content of 15% by weight or less;

(B) 10-90% by weight of a copolymer of propylene and an α -olefin having four or more carbon atoms or a copolymer of propylene, an α -olefin having four or more carbon atoms and ethylene which:

- (i) has a content of the α -olefin having four or more carbon atoms of 8-35 mole%.

- (ii) has an ethylene content of 5 mole% or less,
- (iii) has a cold xylene-soluble portion content of 15-70% by weight, and
- (iv) has a Δ haze of 5% or less; and

(C) 0-15% by weight of a highly crystalline polypropylene having a melting point of 150 °C or more.

5 The polypropylene random copolymer (A) [hereinafter referred to as copolymer (A)] includes known copolymers such as crystalline ethylene-propylene random copolymers and ethylene butene-1/propylene random terpolymers.

The Vicat softening point of copolymer (A) is 122 °C or less, preferably 120 °C or less. The use of a copolymer having a Vicat softening point above 122 °C causes a deterioration in hot tack. Moreover, it becomes necessary to blend in a large amount of copolymer (B) in order to reduce the heat sealing temperature to the target level of the present invention, whereby the blocking resistance, scratch resistance, and slip are deteriorated and the amount of solvent-extractibles becomes large. It has surprisingly been found that when the Vicat softening point of copolymer (A) is 122 °C or less, the heat sealing temperature of a composition consisting of copolymer (A) and a specific copolymer as defined in (B) above becomes much lower than that calculated from the heat sealing temperatures of both on the assumption that an additive effect is obtained from the two.

The amount of the cold xylene-soluble portion of copolymer (A) (hereinafter referred to as the CXS portion) is 15% by weight or less, preferably 13% by weight or less, more preferably 10% by weight or less. When the amount of the CXS portion exceeds the 15% by weight, the blocking resistance and slip are inferior and the amount of the solvent-extractibles becomes large.

20 Copolymer B can be produced by a solvent polymerization in a solvent medium or by a gas phase polymerization. A gas phase polymerization, in which the polymerisation is carried out in the substantial absence of a liquid solvent, is especially preferred for the easy production of a copolymer (B) (having a suitable CXS portion content) and has the advantages that the drying the polymer and/or purifying solvent can be omitted or largely simplified.

Production by a gas phase polymerization can be carried out in a known fluidized bed type reactor, a stirrer-equipped fluidised bed type reactor or the like. The polymerization should be carried out under temperature-pressure conditions that the gas is not liquefied and polymer particles are not melted to form a mass in the reactor. Preferable conditions for the polymerisation are such that the temperature is from 40 °C to 100 °C, preferably 50 °C to 80 °C, and the pressure is from (98-4,900 kPa) (1 to 50 kg/cm²) [gauge, hereinafter referred to as G], preferably (196-1960 kPa G) (2 to 20 kg/cm²). The addition of a molecular-weight regulator such as hydrogen is preferred in order to control the melt fluidity of the polymer obtained. The polymerisation can be carried out batchwise, continuously or as a combination of both. As the monomers and molecular-weight regulator are consumed during the polymerization, fresh starting material can be fed continuously or intermittently into the reactor. Alternatively, a random copolymerization in which the monomers and comonomers are fed simultaneously in a predetermined proportion can be suitably adopted; however, it is possible to alter the proportion of monomers stepwise or continuously with the lapse of time during the polymerization.

40 To remove catalyst residues or low-molecular weight polymers after the polymerization, the reaction product can be washed with an alcohol or a hydrocarbon solvent.

The catalyst system for the production of the copolymer (B) used in the present invention is a known stereoregular polymerization catalyst for α -olefins, namely, a Ziegler-Natta catalyst consisting essentially of a compound of a transition metal of Groups IV-VIII of the periodic Table, an organic compound of a typical metal of Groups I-III of the Periodic Table and a third component such as an electron-donating compound. It is preferable that said transition metal compound or the catalyst component containing said transition metal compound is solid.

The transition metal compound, includes TiCl_3 , which is known to have α , β , γ and δ -type crystal forms. In order to stereoregularly polymerize an α -olefin having three or more carbon atoms, it is preferable to use α , γ or δ -type TiCl_3 which has a layer-like crystal structure. TiCl_3 is generally obtained in the form of a TiCl_3 composition by the reduction of TiCl_4 with hydrogen, metallic aluminum, metallic titanium, an organoaluminum compound or an organomagnesium compound. The preferable TiCl_3 composition is the so-called $\text{TiCl}_3 \cdot \text{AA}$ formed by reducing TiCl_4 with metallic aluminum and then activating it by mechanical grinding. More preferable is a TiCl_3 composition formed by reducing TiCl_4 with an organoaluminum compound and then activating the same with a complexing agent and a halogen compound. Much more preferably used is a trivalent titanium halide containing an alkoxy group(s) obtained by the reduction of $\text{Ti}(\text{OR})_n\text{X}_{4-n}$ (wherein R represents a hydrocarbon group having 1-20 carbon atoms, X a halogen and n is a number of from 0 to 4) with an organoaluminum compound followed by the treatment with an ether compound and TiCl_4 .

The TiCl_3 composition or the alkoxy-containing trivalent titanium halide is preferably such that when the polymerization is effected with a combination thereof with diethylaluminum chloride in the presence of hydrogen in liquefied propylene at 65°C for 4 hours, at least 6,000 g of polypropylene can be produced per gram of the same. Such a TiCl_3 composition can be obtained by a method as disclosed in U.S.P. Nos. 4,210,738 and 4,165,298, Japanese Patent Application "Kokai" (Laid-Open) Nos. 142,904/83 and 28,405/85. Alkoxycontaining trivalent titanium halides can also be obtained by a method as disclosed in Japanese Patent Application "Kokai" (Laid-Open) No. 126,401/84.

When the transition metal compound is used as a catalyst component supported on an appropriate carrier, the carrier includes various solid polymers, especially α -olefin polymers; various organic solid compounds, especially solid hydrocarbons; and various inorganic solid compounds, especially oxides, carbonates and halides. Preferable carriers are magnesium compounds such as the halide, oxide, hydroxide and hydroxyhalide of magnesium. The magnesium compound can be utilized as a complex with the other solid materials mentioned above. As the magnesium compounds, commercially available ones may be used as they are; however, preferred are those obtained by mechanical grinding, by dissolving in a solvent followed by precipitation, by treating with an electron-donating compound or a compound having active hydrogen, or by decomposing an organomagnesium compound such as Grignard reagent. In many cases, it is preferable to use a combination of these operations to obtain the preferable magnesium compound. These operations may be previously conducted in the production of the carrier or the production of the catalyst component. Particularly, preferable magnesium compounds for forming the catalyst carriers are magnesium halides, and particularly preferable transition metal compounds are the above-mentioned titanium halides. The carrier-supported catalyst component comprising titanium, magnesium and halogen as the main ingredients is one of the more preferable catalyst components, which can be produced by a method as disclosed in Japanese patent Application "Kokai" (Laid-Open) Nos. 30,407/81 and 59,915/82. Of these, the carrier-supported catalyst component comprising titanium, magnesium and halogen as the main ingredients and containing an electron-donating compound is one of the much more preferable catalyst components.

Non-carrier-supported type complex catalyst comprising titanium, magnesium, a halogen and an electron-donating compound as the main ingredients is also one of the much more preferable catalyst components, and can be produced by a method as disclosed in Japanese Patent Application No. 59,792/85.

The preferable organic compound of a typical metal of Groups I-III is an organoaluminum compound, especially that represented by the general formula $\text{R}_e\text{AlX}_{3-e}$ (wherein R represents a hydrocarbon group having 1-20 carbon atoms, X is hydrogen or a halogen and e is a number of from 1 to 3). Such compounds include triethylaluminum, triisobutylaluminum, diethylaluminum hydride, diethylaluminum chloride, diethylaluminum bromide, ethylaluminum sesquichloride and ethylaluminum dichloride. The most preferable compounds are triethylaluminum, diethylaluminum chloride and a mixture thereof.

The electron-donating compounds used in the present invention include esters and anhydrides such as ethyl acetate, ϵ -caprolactone, methyl methacrylate, ethyl benzoate, p-ethyl anisate, p-methyl toluylate and phthalic anhydride; ethers such as di-n-butyl ether, diphenyl ether and diglyme; and organophosphorus compounds such as tri-n-butyl phosphite, triphenyl phosphite and hexamethylenephosphoric triamide. Also, usable are ketones, amines, amides, thioethers, alkoxysilanes having Si-O-C linkage, organosilicon compounds such as aryloxysilane.

When, for example, the gas phase polymerization is effected, the solid catalyst component may have previously been treated with a small amount of the olefin in the presence of an organoaluminum compound alone or in combination with an electron-donating compound, prior to the polymerization.

In the copolymer (B) contained in the multi-layer films of the present invention, an α -olefin having 4 or more carbon atoms or a combination of the α -olefin and a very small amount of ethylene is used as comonomers. The α -olefins having four or more carbon atoms, include butene-1, pentene-1, hexene-1, and 4-methylpentene-1, these may be used alone or in admixture of two or more. However, when, for example, the gas phase polymerization is intended, butene-1 is most preferable because it is difficult to liquefy and hence a high partial pressure can be used.

The content of the α -olefin having four or more carbon atoms in the copolymer (B) used in the present invention is 8-35 mole%, preferably 10-30 mole%, more preferably 12-28 mole%. When the α -olefin content is less than said lower limit, the improvement in low-temperature heat sealing property of the multi-layer film becomes insufficient. On the other hand, when the α -olefin content is over said upper limit, the blocking resistance, scratch resistance and slip are deteriorated and the amount of the solvent-extraction in the multi-layer film becomes large.

The ethylene content in the copolymer (B) used in the composition is 5 mole% or less, preferably 3 mole% or less, more preferably 2.5 mole% or less. When the ethylene content is over said upper limit, the

transparency of the multi-layer film is deteriorated with the lapse of time and the blocking resistance and slip are also deteriorated. The reason therefore has not been clarified; however, these deteriorations are considered to be due to the bleed of atactic component.

The amount of the CXS in the copolymer (B) used in the composition is 15-70% by weight, preferably 18-50% by weight, more preferably 18-40% by weight. When the CXS content is lower than said lower limit, the improvement in low-temperature heat sealing property and hot tack of the multi-layer film becomes insufficient. On the other hand, when the CXS content exceeds said upper limit, the blocking resistance, scratch resistance and slip are deteriorated and the amount of the solvent-extraction in the film becomes large.

The Δ haze of the copolymer (B) in the composition used in the present invention is 5% or less, preferably 4% or less, more preferably 3% or less. When the Δ haze is over said upper limit, the improvement in low-temperature heat sealing property of the multi-layer film is insufficient, the transparency is varied with the lapse of time and the blocking resistance and slip are deteriorated.

The amount of the solvent-extraction of the copolymer (B) used in the composition is not critical; however, it is preferably 40% by weight or less, more preferably is 20% by weight or less. The use of the copolymer (B) having a smaller amount of the solvent-extraction than said upper limit is advantageous in that the amount of the solvent-extraction of the composition can be reduced as much even if the proportion of the copolymer (B) blended with copolymer (A) is increased.

The high crystalline polypropylene (C) used in the composition includes known propylene homopolymers or propylene random copolymers containing an extremely small amount of a comonomer, preferably those having a CXS content of 5% by weight or less. The melting point of said high crystalline polypropylene is 150°C or more, preferably 155°C or more. When the melting point is lower than said lower limit, the improvement in blocking resistance and slip of the multi-layer film is poor. The present inventors have surprisingly found that when said highly crystalline polypropylene (C) is added in a small amount, the blocking resistance and slip are greatly improved with almost no adverse effect on transparency and heat sealing temperature.

The composition used in the present invention comprises 10-90% by weight of the copolymer (A), 10-90% by weight of the copolymer (B) and 0-15% by weight of the highly crystalline polypropylene (C), preferably 10-90% by weight of the copolymer (A), 10-90% by weight of the copolymer (B), and 1-15% by weight of the highly crystalline polypropylene (C), more preferably 15-85% by weight of the copolymer (A), 10-85% by weight of the copolymer (B) and 2-10% by weight of the highly crystalline polypropylene (C).

When the proportion of the copolymer (A) blended is over said upper limit, the proportion of the copolymer (B) blended becomes necessarily decreased as much and, as a result, the target level of low-temperature heat sealing property of the multi-layer film cannot be attained. When the proportion of the copolymer (A) blended is lower than said lower limit, the proportion of the copolymer (B) blended and the amount of the solvent-extraction become necessarily increased as much.

When the proportion of the copolymer (B) blended is over said upper limit, the blocking resistance and slip are deteriorated and the amount of the solvent-extraction is increased even if the highly crystalline polypropylene (C) is added. On the other hand, when the proportion of the copolymer (B) blended is lower than said lower limit, the target level of the low-temperature heat sealing property of the multi-layer film cannot be attained.

When the proportion of the highly crystalline polypropylene (C) exceeds said upper limit, the low-temperature heat sealing property and transparency are deteriorated. The proportion of the highly crystalline polypropylene (C) blended may be zero; however, in such a case, the improvement in blocking resistance and slip is not so great, and hence, it is preferable to blend the same in an amount lower than said upper limit.

The preferable range of the melt index (g/10 min) of the composition is 0.5-10 g/10 min. A composition having a melt index lower than said lower limit is unsuitable because of its poor processability, whereas a composition having a melt index over said upper limit is also unsuitable because of its low heat sealing strength.

It is preferable for the above-mentioned composition to have a main peak appearing in the range of from 127°C to 140°C and a subpeak appearing in each of the ranges of from 95°C to 127°C and from 147°C to 160°C on a fusion curve as measured by DSC (differential scanning calorimetry). The absence of subpeak between 95°C and 127°C is unsuitable because the low-temperature heat sealing property is poor, whereas the absence of subpeak between 147°C and 160°C causes little improvement in blocking resistance and slip.

The above-mentioned composition can be obtained by a homogeneous dispersion according to any known method, for example, the meltextrusion blending or the Banbury blending. Also, it can be obtained

by so-called multi-step polymerization, in which the polymerization conditions are stepwise changed.

Additives such as antistatic agent, antiblocking agent, slipping agent, stabilizer and nucleus forming agent can be added to the composition.

A polypropylene multi-layer film of the present invention can be obtained by laminating the above-mentioned heat sealing resin composition to one or both sides of the crystalline polypropylene film as a substrate according to any known method. That is, the multi-layer film of the present invention can be obtained by passing a substrate film and a sheet made of a heat sealing resin layer with an adhesive through between pressure rollers; by coating the substrate film with a heat sealing resin in the form of a solution in a solvent such as toluene or a dispersion; by melt-extruding and coating a heat sealing resin on the substrate film; or by extruding a heat sealing resin and a substrate polymer by respective extruders followed by joining the two in the molten state in the common die or at the exit.

It is preferable that the heat seal layer of the multi-layer film of the present invention is stretched in at least one direction. The stretched polypropylene multi-layer film is obtained according to the following known method:

1. A method consisting of the steps of producing an original laminate sheet by the so-called co-extruding that the substrate and the resin composition are joined in a molten state in the die or near the exit, and biaxially stretching the same.
2. A method consisting of the steps of extrusion-laminating the heat sealing resin to the polypropylene substrate sheet and biaxially stretching the same.
3. A method consisting of the steps of extrusion-laminating the heat sealing resin to the polypropylene substrate sheet previously stretched in the machine direction uniaxially in a heated state by a group of rollers containing one or more pairs of metal rollers and stretching the same in the transverse direction.

The polypropylene multi-layer film thus obtained has not only a remarkably excellent low-temperature heat sealing property but also an excellent transparency, scratch resistance and hot tack, and a small amount of the solvent-extraction. It is suited for, for example, food contact uses. Further, in a more preferable mode, it also has an excellent slip and blocking resistance. It has the markedly great practical value that the production cost is low.

The data and valuations in the following Examples and Comparative Examples were obtained as follows:

(1) α -olefin content in copolymer

α -olefin content in copolymer was estimated from the material balance. As to butene-1 content, the result from the material balance was confirmed by the conventional measurement using the infrared spectrophotometer with the characteristic absorption at 770 cm^{-1} . The measurement was carried out by utilizing the analytical curve obtained by the quantitative data of propylene-butene-1 copolymer by ^{13}C -NMR.

(2) Ethylene content in copolymer

Ethylene content in copolymer was estimated from the material balance. The result was confirmed by the conventional measurement using the infrared spectrophotometer with the characteristic absorption at 732 and 720 cm^{-1} . The measurement was carried out by utilizing the analytical curve obtained by the quantitative data of the radiation measurement of ^{14}C -labeled ethylene copolymer.

(3) Melt Index (MI)

The melt index was measured in accordance with ASTM-D1238.

(4) Vicat softening point (VSP)

The Vicat softening point was measured in accordance with ASTM-D1525.

(5) Cold xylene-soluble content (CXS) (% by weight)

5 g of polymer was dissolved in 500 ml of xylene, and then was cooled gradually to the room temperature. After allowing it stand in a bath at 20°C for four hours, it was filtered. The filtrate was concentrated, dried up and weighed.

(6) Intrinsic viscosity ($[\eta]$)

Viscosities were measured with a conventional method in tetralin at 135 °C on diluted samples having a concentration of 0.4, 0.2, 0.133 or 0.1 g/dl.

(7) Δ Haze

The Δ Haze was indicated by the difference between the haze values before and after the annealing of the press sheet of the copolymer having a thickness of 100 μ m for 9 hours at 60 °C.

(8) Amount of solvent-extraction

The amount of solvent-extraction was indicated by the amount of material extracted with n-hexane at 50 °C prescribed in FDA § 177.1520.

(9) Melting point (T_m)

The melting point was measured by the differential scanning calorimeter. After the annealing of the samples for 5 minutes at 200 °C followed by the cooling and solidification at the rate of 10 °C/min, the measurement was carried out in the condition of increasing rate of 20 °C/min.

As the data of the melting point, not only the temperature giving the highest peak (main peak temperature) but also the temperatures giving definitely the maximum peaks (subpeak temperatures) were described.

(10) Haze

The haze was measured in accordance with ASTM-D1003.

(11) Heat sealing temperature

Two portions of the films were superposed face to face and pressure-bound by means of heat sealer heated at a prescribed temperature under a load of (196 kPa) (2 kg/cm² G) for 2 seconds to obtain a specimen of 25 mm width. The peeling resistance of this specimen was measured under the condition of peeling velocity of 200 mm/min. and peeling angle of 180°. The temperature when the peeling resistance reached 300 g/25 mm was defined as the heat sealing temperature.

(12) Slip (μ_s/μ_k)

The slip was measured in accordance with ASTM-D1894. (μ_s : coefficient of static friction, μ_k : coefficient of kinetic friction)

(13) Blocking

A specimen suffered blocking by treating it at 60 °C for 3 hours under a load of (49 kPa) (500 g/12 cm²). Then the specimen was subjected to a shear tensile test to determine the largest load (kg) to peel the specimen and it was indicated by unit of (8.2 kPa) (kg/12 cm²).

(14) Scratch resistance

A heat sealing resin-laminated side of a multi-layer film was scratched violently with nails. The degree of scratch was indicated by three grades (O, Δ , X).

The present invention will be further illustrated below with reference to Examples and Comparative Examples to be more clearly understood. However, the Examples and the Comparative Examples are not by way of limitation but by way of illustration.

Example 1

(1) Synthesis of solid product

Atmosphere in a 500 ml-flask equipped with a stirrer and a dropping funnel was replaced with argon. Then there were charged 83 ml of n-heptane, 16.1 ml of titanium tetrachloride and 51.0 ml of titanium tetra-n-butoxyde. With stirring, the temperature of the mixture in the flask was kept at 20 °C. A solution consisting of 162.1 ml of n-heptane and 37.8 ml of diethylaluminum chloride was gradually fed by the dropping funnel for 3 hours maintaining the temperature of the mixture in the flask at 20 °C. After the completion of the feed, the temperature was raised up to 50 °C and the mixture in the flask was stirred for an hour. Then the flask was allowed to stand at room temperature to separate solid from liquid. After washing the solid four times with 200 ml of n-heptane, it was dried under reduced pressure to obtain 64.7 g of red brown solid product.

10 (2) Synthesis of preliminarily polymerized solid

Atmosphere in a stirrer-equipped 300 ml-flask was replaced with argon. Then there were charged 241 ml of n-heptane, 0.34 g of triethylaluminum and 19.7 g of solid product prepared in above (1) with maintaining the temperature of the suspension at 50 °C. With stirring the suspension, ethylene was gradually fed keeping its partial pressure of (19.6 kPa) (0.2 kg/cm²) to the suspension for 20 minutes at 50 °C to carry out the preliminary polymerization treatment. After the completion of the treatment, solid was separated from liquid. The solid was washed twice with 50 ml of n-heptane, then dried under reduced pressure. 0.09 g of preliminarily polymerized solid was obtained per gram of the solid product.

20 (3) Synthesis of solid catalyst component

Atmosphere in 100 ml-flask was replaced with argon. Then, 12.1 g of the preliminarily polymerized solid prepared in above (2) and 42.3 ml of n-heptane were charged into the flask, and the temperature thereof was kept at 30 °C. Next, 14.4 ml of di-isoamyl ether was added thereto. After the mixture was treated at 30 °C for an hour, the temperature thereof was raised up to 75 °C. Then, 15.7 ml of titanium tetrachloride was added, and the reaction was carried out at 75 °C for an hour. The resulting solid was separated from liquid. The solid was washed four times with 50 ml of n-heptane, then dried under reduced pressure to obtain a solid component. Further, atmosphere in 100 ml-flask was replaced with argon, and then 9.9 g of the above solid component and 38 ml of n-heptane were charged thereto, and the temperature thereof was kept at 30 °C. Next, 8.5 ml of di-isoamyl ether was added thereto. After the treatment at 30 °C for an hour, the temperature was raised up to 75 °C. Then, 11.5 ml of titanium tetrachloride was added thereto and the reaction was carried out at 75 °C for an hour. The resulting solid was separated from liquid. The solid was washed four times with 50 ml of n-heptane, then dried under reduced pressure to obtain a solid catalyst component.

35 (4) Copolymerization [Copolymer (B)]

Copolymerization of propylene and butene-1 was carried out utilizing a stirrer-equipped fluid bed reactor having an internal volume of 1 m³ as follows. 60 kg of particles of propylene-butene-1 copolymer for dispersing catalyst was fed into the reactor, then the atmosphere thereof was replaced with nitrogen and then with propylene. The pressure was raised by injecting propylene up to (490 kPa) (5 kg/cm² G). To the bottom of the reactor, recycling gas was fed at a flow rate of 80 m³/h to maintain the polymer particles to be in flux. Then the following catalysts were charged into the reactor.

- (a) solid catalyst component 21 g
- (b) diethylaluminum chloride 156 g
- (c) triethylaluminum 22 g
- (d) methyl methacrylate 15 g

Catalyst components (b) and (c) diluted with heptane were used. Then hydrogen, propylene and butene were fed so as to give a hydrogen concentration of 1.7% by volume and a butene-1 concentration of 29% by volume. And the total pressured was raised up to (980 kPa) (10 kg/cm² G). Controlling the temperature of the fluidized bed at 70 °C, the polymerization was started. During the polymerization, hydrogen, propylene and butene-1 were fed so as to maintain the constant concentrations and partial pressures of hydrogen and butene-1. When the amount of polymerized polymer reached to 75 kg, the polymer particles in the reactor, except 60 kg thereof for the catalyst dispersion for the next polymerization, were transferred into vessel. Then it was dried to obtain white powdery polymer. The same polymerization was repeated three times, and the characteristics of the polymer obtained in the third polymerization [Copolymer (B)] were evaluated. The results were that butene-1 content was 20.3 mole%, the CXS content was 23.9%, Δhaze was 0.9%, the amount of solvent-extraction was 7.3% and the intrinsic viscosity was 1.8 dl/g.

(5) Preparation of composition

① Copolymer (A)

5 Sumitomo Noblen® RW160 (a registered trade mark, mfd. by Sumitomo Chemical Co., Ltd.) was used. It had an ethylene content of 4.8% by weight, a Vicat softening point of 118°C, a melt index of 8.8 g/10 min and a CXS content of 4.3% by weight.

② highly crystalline polypropylene (C)

10 Sumitomo Noblen® HS200A (a registered trade mark, mfd. by Sumitomo Chemical Co., Ltd.) was used. It had a melting point of 161°C, a melt index of 1.8 g/10 min and a CXS content of 2.8% by weight.

65% by weight of above copolymer (A), 30% by weight of copolymer (B) obtained in (4) and 5% by weight of above highly crystalline polypropylene (C) were meltblended uniformly with a 65 mmφ extruder. 15 Thereto were added 0.2 PHR (parts per hundred of resin) of BHT (2,6-di-*t*-butyl-4-hydroxytoluene) as anti-oxidant, 0.2 PHR of silica as anti-blocking agent and 0.2 PHR of stearic acid amide as slipping agent.

(6) Lamination and stretching

20 The composition obtained in (5) was laminated to a homopolypropylene sheet having a thickness of 500 μm by press molding so that the layer of the composition gives a thickness of 100 μm. (The thickness of the multi-layer sheet was 600 μm).

Then, a specimen 90 mm square taken from the said multi-layer sheet was subjected to a stretching under the following conditions to obtain a biaxial-stretched film.

25 Stretching machine: bench biaxial stretching machine mfd. by Toyo Seiki Co., Ltd.

Temperature : 150°C

Preheating time : 3 min

Stretching ratio : 5 times for the machine direction
5 times for the transverse direction

30 Stretching velocity: 5 m/min.

The properties of the above-obtained multi-layer stretched film having a thickness of 24 μm are shown in Table 1. This multi-layer stretched film had not only a remarkably low heat sealing temperature but also an excellent transparency, slip, blocking resistance and scratch resistance.

35 Examples 2, 3 and 4

Using the copolymer (A), copolymer (B) and highly crystalline polypropylene (C) as same as in Example 1, multi-layer stretched films were obtained under the same conditions as in Example 1 except that the proportions in the compositions were altered. The proportions are shown in Table 1.

40 These multi-layer stretched films had excellent properties as in Example 1.

Example 5

(1) Polymerization of copolymer (B)

45 Using the same catalyst system as in Example 1, a copolymer was obtained under the same polymerization conditions as in Example 1 except that the charged amounts of butene-1 and so on were altered. The obtained copolymer (B) had the butene-1 content of 15.8 mole%, the CXS content of 19.5% by weight, Δhaze of 0.4%, the amount of solvent-extraction of 6.2% and the intrinsic viscosity of 1.8 dl/g.

50

(2) Preparation of composition and production of multi-layer film

① Copolymer (A)

55 Sumitomo Noblen® FL6711N (a registered trade mark, mfd. by Sumitomo Chemical Co., Ltd.) was used. It has an ethylene content of 6.2% by weight, a Vicat softening point of 109°C, a melt index of 5.5 g/10 min and a CXS content of 9.5%.

② Highly crystalline polypropylene (C)

The same highly crystalline polypropylene as in Example 1 was used.

A multi-layer stretched film was obtained under the same conditions as in Example 1 except that 15% by weight of above copolymer (A), 75% by weight of copolymer (B) obtained in (1) and 10% by weight of above highly crystalline polypropylene (C) were compounded.

This multi-layer stretched film had excellent properties as in Example 1.

Example 6

10

Using the copolymer (A), the copolymer (B) and the highly crystalline polypropylene (C) as same as in Example 5, a multi-layer stretched film was obtained under the same conditions as in Example 1 except that the proportion of the composition was altered. The proportion is shown in Table 1.

This multi-layer stretched film had excellent properties as in Example 1.

15

Example 7

(1) Polymerization of copolymer (B)

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Using the catalyst system as same as in Example 1, a copolymer was obtained under the same polymerization conditions as same as in Example 1 except that the charged amount of butene-1 were altered and that the pressure at the polymerization was altered to (686 kPa) (7 kg/cm² G). The copolymer (B) obtained had the butene-1 content of 25.1 mole%, the CXS content of 35.1% by weight, the Δ haze of 1.6%, the amount of solvent-extraction of 15.5% and the intrinsic viscosity of 2.0 dl/g.

25

(2) Preparation of composition and production of multi-layer film

① Copolymer (A)

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The same copolymer as in Example 1 was used.

② Highly crystalline polypropylene (C)

The same highly crystalline polypropylene as in Example 1 was used.

35

A multi-layer stretched film was obtained under the same conditions as same as in Example 1 except that 81% by weight of above copolymer (A), 15% by weight of copolymer (B) obtained in (1) and 4% by weight of above highly crystalline polypropylene (C) were compounded. This multilayer stretched film had excellent properties as in Example 1.

40

Example 8

(1) Polymerization of copolymer (B)

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Using the same catalyst system as in Example 1 except that triethylaluminum was not contained and that the amount used of methyl methacrylate was decreased to 8 g, a copolymer was obtained under the same polymerization conditions as in Example 1 except that the charged amount of butene-1 was altered and that ethylene was newly introduced into the reaction. The obtained copolymer (B) had the butene-1 content of 16.1 mole%, the ethylene content of 2.0 mole%, the CXS content of 24.5%, the Δ haze of 1.3%, the amount of solvent-extraction of 12.5% and the intrinsic viscosity of 2.0 dl/g.

50

(2) Preparation of composition and production of multi-layer film

① Copolymer (A)

55

The same copolymer as in Example 1 was used.

② Highly crystalline polypropylene (C)

The same highly crystalline polypropylene as in Example 1 was used. A multi-layer stretched film was obtained under the same conditions as in Example 1 except that 65% by weight of above copolymer (A), 30% by weight of copolymer (B) obtained in (1) and 5% by weight of above highly crystalline polypropylene (C) were compounded. This multi-layer film had excellent properties as in Example 1.

5
Example 9

Using the copolymer (A) and copolymer (B) as same as in Example 1, a multi-layer stretched film was obtained under the same conditions as in Example 1 except that the proportion of the composition was altered.

This composition had a low amount of solvent-extraction and the multi-layer stretched film comprising this composition had an excellent transparency, low-temperature heat sealing property and scratch resistance.

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Example 10

(1) Polymerization of copolymer (B)

Using the same catalyst system as in Example 1, a copolymer was obtained under the same polymerization conditions as those in Example 1 except that 4-methyl-1-pentene was newly added and the charged monomer proportions were changed. The content of an α -olefin in the copolymer was 17.1 mole% (content of butene-1, 14.0 mole%; content of 4-methyl-1-pentene, 3.1 mole%), the CXS was 26.3% by weight, the Δ haze of 0.4%, the amount of solvent-extraction of 8.5% by weight and the intrinsic viscosity of 1.8 dl/g.

25
(2) Preparation of composition and production of multilayer film

① Copolymer (A)

30 The same copolymer as in Example 1 was used.

② Highly crystalline polypropylene (C)

The same highly crystalline polypropylene as in Example 1 was used.

35 A multi-layer stretched film was obtained under the same conditions as in Example 1 except that 65% by weight of above copolymer (A), 30% by weight of copolymer (B) obtained above in (1) and 5% by weight of above highly crystalline polypropylene (C) were compounded. This multi-layer film had excellent properties as in Example 1.

40 Comparative Example 1

Using the same copolymer (A), copolymer (B) and highly crystalline polypropylene (C) as in Example 1, a multi-layer stretch film was obtained under the same conditions as in Example 1 except that the proportion of the composition was altered. The proportion is shown in Table 1. This multi-layer film was not only unsatisfactory in low-temperature heat sealing property but also unsuitable in transparency.

Comparative Example 2

(1) Preparation of composition and production of multi-layer film

50
① Copolymer (A)

Sumitomo Noblen® RW140 (a registered trade mark, mfd. by Sumitomo Chemical Co., Ltd.) was used. It had the ethylene content of 3.7% by weight, the Vicat softening point of 125°C, the melt index of 8.3 g/10 min and the CXS content of 3.8%.

② Copolymer (B) and highly crystalline polypropylene (C)

Those which are the same as in Example 1 were used.

A multi-layer stretched film was obtained under the same conditions as in Example 1 except that 75% by weight of above copolymer (A), 20% by weight of above copolymer (B) and 5% by weight of above highly crystalline polypropylene (C) were compounded. It was evident that this multi-layer stretched film was greatly inferior in low-temperature heat sealing property compared with that in Example 2. From this fact, it is clear that a very unique effect is caused only by compounding copolymer (A) within the range defined in the present invention.

Comparative Example 3

10

(1) Preparation of composition and production of multi-layer film

① Copolymer (A)

15

Sumitomo Noblen® RW120 (a registered trade mark, mfd. by Sumitomo Chemical Co., Ltd.) was used. It had the ethylene content of 2.3% by weight, the Vicat softening point of 137° C, the melt index of 9.1 g/10 min. and the CXS content of 3.2%.

② Copolymer (B)

20

Tafmer® (a registered trade mark, mfd. by Mitsui petrochemical Industries Ltd.), a propylene-butene-1 random copolymer, was used. It had the butene-1 content of 26.5 mole%, the CXS content of 62%, the Δ haze of 2.5%, the amount of solvent-extraction of 69% by weight and the intrinsic viscosity of 1.8 dl/g.

A multi-layer stretched film was obtained under the same conditions as in Example 1 except that 40% by weight of above copolymer (A) and 60% by weight of above copolymer (B) were compounded. This film was unsuitable because it was inferior in scratch resistance and the amount of solvent-extraction of the composition was very large though it is satisfactory in low-temperature heat sealing property.

Comparative Example 4

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(1) Preparation of composition and production of multi-layer film

① Copolymer (A) and copolymer (B)

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Those which are the same as in Example 1 were used.

A multi-layer stretched film was obtained under the same conditions as in Example 1 except that 95% by weight of above copolymer (A) and 5% by weight of above copolymer (B) were compounded. This multi-layer stretched film was unsuitable because of its poor low-temperature heat sealing property.

Comparative Example 5

(1) Preparation of composition and production of multi-layer film

① Copolymer (A)

45

The same copolymer (A) as in Example 1 was used.

② Copolymer (B)

50

A propylene-butene-1 copolymer obtained by the slurry polymerization using n-heptane as a solvent followed by reducing n-heptane soluble parts was used. It had the butene-1 content of 15.1 mole%, the CXS content of 10.1% by weight, the Δ haze of 0.5%, the amount of solvent-extraction of 3.0% by weight and the intrinsic viscosity of 1.9 dl/g.

A multi-layer film was obtained under the same conditions as in Example 1 except that 70% by weight of above copolymer (A) and 30% by weight of above copolymer (B) were compounded. This multi-layer film was unsuitable because of its poor low-temperature heat sealing property.

Comparative Example 6

Using the same copolymer (B) as used in Example 5 alone, a multi-layer stretched film was obtained under the same conditions as in Example 1. This copolymer (B) had so large amount of solvent-extraction that it did not meet the object of the present invention.

5 Comparative Example 7

Using the same copolymer (A) as used in Example 1 alone, a multi-layer stretched film was obtained under the same conditions as in Example 1. This multi-layer film had an extremely poor low-temperature heat sealing property.

10

Comparative Example 8

(1) Polymerization of copolymer (B)

15 Using the same catalyst system as in Example 1, a copolymer was obtained under the same polymerization conditions as those in Example 1 except that the charged amount of butene-1 was altered and that ethylene was newly introduced into the reaction. The obtained copolymer (B) had the butene-1 content of 8.1 mole %, the ethylene content of 6.1 mole %, the CXS content of 22.5%, the Δ haze of 8.3%, the amount of solvent-extraction of 8.5% by weight and the intrinsic viscosity of 1.7 dl/g.

20

(2) Preparation of composition and production of multilayer film

1 Copolymer (A)

The same copolymer as in Example 5 was used.

25

2 Highly crystalline polypropylene (C)

The same highly crystalline polypropylene as in Example 1 was used.

30

A multi-layer stretched film was obtained under the same conditions as in Example 1 except that 15% by weight of above copolymer (A), 75% by weight of copolymer (B) obtained above in (1) and 10% by weight of above highly crystalline polypropylene (C) were compounded. The transparency of this multi-layer stretched film became worse in the passage of time. Moreover, it was inferior in low-temperature heat sealing property, slip and blocking resistance.

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Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5
proportion (wt%)					
(A)	65	75	37	78	15
(B)	30	20	55	20	75
(C)	5	5	8	2	10
MI (g/10 min.)	7.7	8.1	6.8	8.2	5.4
amount of solvent-extraction (wt%)	1.6	1.4	2.9	1.4	3.9
melting point (°C)	109 140 150	111 139 150	108 139 151	110 138 148	115 146 155
haze (%)	1.0	1.1	1.4	0.7	1.5
heat sealing temperature (°C)	90	99	86	98	95
μs/μk	0.81/0.84	0.75/0.78	0.87/0.89	0.88/0.90	0.69/0.72
blocking μg/cm² ^{kg/12 cm²}	0.19 (1.55)	0.13 (1.06)	0.25 (2.04)	0.34 (2.72)	0.10 (0.82)
scratch resistance	o	o	o	o	o

- Cont'd -

Table 1 (Cont'd)

Example 6	Example 7	Example 8	Example 9	Example 10	Comparative Example 1	Comparative Example 2
70	81	65	70	65	27	75
25	15	30	30	30	55	20
5	4	5	0	5	18	5
8.0	8.5	7.2	7.9	7.8	4.9	7.9
2.3	1.8	2.9	2.1	2.0	2.5	1.3
115 141 152	112 139 149	108 139 150	109 138	108 142 151	115 148 156	117 145 152
1.1	0.9	1.0	0.7	1.2	3.5	1.2
100	93	89	89	91	104	121
0.80/0.80	0.90/0.92	0.85/0.89	>1.6/>1.6	0.85/0.88	0.5/0.53	0.71/0.75
(0.18) (1.42)	0.32 (2.22)	0.22 (7.92)	>2.0 (11.3)	0.21 (1.22)	<0.1 (46.32)	0.12 (0.71)
0	0	0	0	0	0	0

Table 1 (Cont'd)

Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
40	95	70	0	100	15
60	5	30	100	0	75
0	0	0	0	0	10
7.6	8.6	7.5	5.5	8.8	7.5
10.2	1.2	1.4	6.2	1.1	4.9
111 148	137	112 139	107 136 146	137	118 140 154
0.7	0.8	0.7	1.3	0.7	2.5
89	125	115	92	131	110
>1.6/>1.6	1.5/1.4	1.2/1.2	1.5/1.5	1.4/1.3	1.5/1.4
>2.0 (2.16.3)	0.51 (4.12)	0.65 (5.1)	0.71 (8.6)	0.35 (1.16)	>2.0 (2.16.3)
Δ	0	0	0	0	0

Claims

1. A multi-layer polypropylene film which comprises a crystalline polypropylene substrate layer having laminated to at least one side thereof a sheet of a resin composition comprising:
(A) 10-90% by weight of a propylene random copolymer which:

- (i) has a comonomer content of 4-15% by weight,
- (ii) has Vicat softening point of 122 °C or less,
- and
- (iii) has a cold xylene-soluble portion content of 15% by weight or less;
- 5 (B) 10-90% by weight of a copolymer of propylene and an α -olefin having four or more carbon atoms or a copolymer of propylene, an α -olefin having four or more carbon atoms and ethylene, which:
 - (i) has a content of the α -olefin having four or more carbon atoms of 8-35 mole%.
 - (ii) has an ethylene content of 5 mole% or less,
 - 10 (iii) has a cold xylene-soluble portion content of 15-70% by weight, and
 - (iv) has a Δ haze of 5% or less; and
 - (C) 0-15% by weight of a highly crystalline polypropylene having a melting point of 150 °C or more.
- 2. A multi-layer film as claimed in claim 1, characterized in that the amount of solvent-extractibles in
- 15 copolymer (B) is 40% by weight or less.
- 3. A multi-layer film as claimed in claim 1 or claim 2, characterized in that the resin composition comprises 10-90% by weight of copolymer (A), 10-90% by weight of copolymer (B) and 1-15% by weight of highly crystalline polypropylene (C).
- 20 4. A multi-layer film as claimed in any one of claims 1-3 characterised in that the fusion curve, as measured by differential scanning calorimetry, has a main peak appearing in the range of from 127 ° to 147 °C and a subpeak appearing in each of the ranges of from 95 ° to 127 °C and from 147 °C to 160 °C.
- 25 5. A multi-layer film as claimed in any one of the preceding claims characterized in that the α -olefin of copolymer (B) is butene-1, pentene-1, hexene-1, and/or 4-methylpentene-1.
- 6. A multi-layer film as claimed in claim 5 characterized in that the α -olefin of copolymer (B) is butene-1.
- 30 7. A multi-layer film as claimed in any one of the preceding claims characterized in that the multi-layer film is stretched in at least one direction.
- 8. A multi-layer film as claimed in claim 7 characterized in that the multi-layer film is biaxially stretched.

Revendications

- 1. Film à base de polypropylène multi-couches, qui comprend une couche substrat en polypropylène cristallin sur au moins une face de laquelle est contrecollée une feuille d'une composition de résine
- 40 comprenant
 - (A) 10 à 90% en poids d'un copolymère statistique de propylène qui
 - (i) a une teneur en comonomère de 4-15% en poids,
 - (ii) a un point de ramollissement Vicat de 122 °C ou moins,
 - et
 - 45 (iii) a une teneur en portion soluble dans le xylène froid de 15% en poids ou moins;
 - (B) 10 à 90% en poids d'un copolymère de propylène et d'une α -oléfine ayant quatre atomes de carbone ou plus ou d'un copolymère de propylène, d'une α -oléfine ayant quatre atomes de carbone ou plus et d'éthylène, qui
 - (i) a une teneur en α -oléfine ayant quatre atomes de carbone ou plus de 8-35% en moles,
 - 50 (ii) a une teneur en éthylène de 5% en moles ou moins,
 - (iii) a une teneur en portion soluble dans le xylène froid de 15-70% en poids, et
 - (iv) a un Δ trouble de 5% ou moins; et
 - (C) 0-15% en poids d'un polypropylène hautement cristallin ayant un point de fusion de 150 °C ou plus.
- 55 2. Film multi-couches selon la revendication 1, caractérisé en ce que la quantité de matières extractibles par solvant dans le copolymère (B) est 40% en poids ou moins.

3. Film multi-couches selon la revendication 1 ou la revendication 2, caractérisé en ce que la composition de résine comprend 10-90% en poids de copolymère (A), 10-90% en poids de copolymère (B) et 1-15% en poids de polypropylène hautement cristallin (C).
- 5 4. Film multi-couches selon l'une quelconque des revendications 1 à 3, caractérisé en ce que la courbe de fusion, telle que déterminée par calorimétrie à balayage différentielle, a un pic principal apparaissant entre 127° et 147° C et un pic secondaire apparaissant entre 95° et 127° C et entre 147° et 160° C.
- 10 5. Film multi-couches selon l'une quelconque des revendications précédentes, caractérisé en ce que l' α -oléfine du copolymère (B) est le butène-1, le pentène-1, l'hexène-1 et/ou le 4-méthylpentène-1.
6. Film multi-couches selon la revendication 5, caractérisé en ce que l' α -oléfine du copolymère (B) est le butène-1.
- 15 7. Film multi-couches selon l'une quelconque des revendications précédentes, caractérisé en ce que le film multi-couches est étiré (orienté) dans au moins une direction.
8. Film multi-couches selon la revendication 7, caractérisé en ce que le film multi-couches est étiré biaxialement.

Patentansprüche

1. Mehrschicht-Polypropylenfolie, umfassend eine kristalline Polypropylen-Substratschicht, die auf mindestens einer ihrer Seiten auflaminiert eine Schicht aus einer Harzmasse aufweist, welche umfaßt:
 - 25 (A) 10 bis 90 Gew.-% eines statistischen Propylen-Copolymerisates, welches
 - (i) einen Comonomergehalt von 4 bis 15 Gew.-% hat,
 - (ii) einen Vicat-Erweichungspunkt von höchstens 122° C hat, und
 - (iii) einen Gehalt an in kaltem Xylol löslichem Anteil von höchstens 15 Gew.-% aufweist;
 - 30 (B) 10 bis 90 Gew.-% eines Copolymerisates von Propylen und einem α -Olefin mit mindestens 4 Kohlenstoffatomen oder eines Copolymerisates von Propylen, einem α -Olefin mit mindestens 4 Kohlenstoffatomen und Ethylen, welches:
 - (i) einen Gehalt des α -Olefins mit mindestens 4 Kohlenstoffatomen von 8 bis 35 Mol-% hat,
 - (ii) einen Ethylengehalt von höchstens 5 Mol-% hat,
 - (iii) einen Gehalt an in kaltem Xylol löslichem Anteil von 15 bis 70 Gew.-% aufweist, und
 - 35 (iv) eine Δ Trübung von höchstens 5 % besitzt; und
 - (C) 0 bis 15 Gew.-% eines hochkristallinen Polypropylens mit einem Schmelzpunkt von mindestens 150° C.
- 40 2. Mehrschichtfolie nach Anspruch 1, **dadurch gekennzeichnet**, daß die Menge an Lösungsmittel extrahierbaren Bestandteilen im Copolymerisat (B) höchstens 40 Gew.-% beträgt.
3. Mehrschichtfolie nach Anspruch 1 oder Anspruch 2, **dadurch gekennzeichnet**, daß die Harzmasse 10 bis 90 Gew.-% Copolymer (A), 10 bis 90 Gew.-% Copolymer (B) und 1 bis 15 Gew.-% hochkristallines Polypropylen (C) umfaßt.
- 45 4. Mehrschichtfolie nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet**, daß die Schmelzkurve, gemessen durch differentielle Rastercalorimetrie, einen Haupt-Peak im Bereich von 127 bis 147° C und einen Unter-Peak jeweils im Bereich von 95 bis 127° C und von 147 bis 160° C aufweist.
- 50 5. Mehrschichtfolie nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet**, daß das α -Olefin des Copolymerisates (B) Buten-1, Penten-1, Hexen-1 und/oder 4-Methylpenten-1 ist.
6. Mehrschichtfolie nach Anspruch 5, **dadurch gekennzeichnet**, daß das α -Olefin des Copolymerisats (B) Buten-1 ist.
- 55 7. Mehrschichtfolie nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet**, daß die Mehrschichtfolie in mindestens einer Richtung verstreckt ist.

8. Mehrschichtfolie nach Anspruch 7, **dadurch gekennzeichnet**, daß die Mehrschichtfolie biaxial verstreckt ist.

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EP-A- 0 146 968
EP-A- 0 217 598
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